

# Isotope analysis of hydrocarbons: trapping, recovering and archiving hydrocarbons and halocarbons separated from ambient air

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It is argued that isotope analysis of atmospheric non-methane hydrocarbons (NMHCs) and, in particular, the analysis of the deuterium/hydrogen (D/H) ratio is valuable because the dominant self-cleansing property of the troposphere is based on the OH radical which removes, e.g., CH<sub>4</sub> and other alkanes by H-atom abstraction, which induces large kinetic isotope effects. The major obstacle in applying D/H isotope analysis to atmospheric NMHCs is not only the low abundance of D itself but, in particular, the low concentrations of NMHCs in the parts per trillion range. We show how a selection of NMHCs can be quantitatively separated from 300 L air samples together with CO<sub>2</sub> as carrier gas matrix, by using high efficiency cryogenic traps. After diluting the extracted NMHC mixtures with hydrocarbon free air, and determining the mixing ratios, good agreement with original whole air sample analysis exists for alkanes and several halocarbons. For unsaturated hydrocarbons and some other halocarbons the extraction and recovery yield under the given conditions fell considerably, as a function of boiling point. Furthermore, the mixture of NMHCs in the CO<sub>2</sub> matrix is proven to remain unchanged over several years when conveniently stored in glass ampoules. The 'extracts' or 'concentrates' of condensables extracted from larger air samples will enable the D/H isotope analysis of ultra trace gases in the atmosphere. Copyright © 2005 John Wiley & Sons, Ltd.

The interest in atmospheric non-methane hydrocarbons (NMHCs, comprising alkanes, alkenes, alkynes, terpenes, and aromatic compounds from C<sub>2</sub> to about C<sub>16</sub>) is driven by three aspects. First of all, NMHCs provide a large—partly systematic—series of chemical tracers derived from a wide range of natural and man-made sources, namely vegetation, oceans, biomass burning, and the use of fossil fuels and derived solvents.<sup>1–9</sup> By measuring NMHCs, their sources can be identified due to the detailed fingerprint provided. Secondly, their reactivity with the OH radical, which is mostly based on H-atom extraction, provides a means of estimating the 'exposure age' of a given air mass to the oxidative workings of OH.<sup>10–12</sup> Depending on the latitude and season, the atmospheric residence times of the NMHCs span a range from a few minutes to several months.<sup>13–15</sup> Moreover, measurements of certain NMHCs have been used to assess the abundance of free Cl radicals.<sup>16,17</sup> This is of importance because direct measurement of Cl radicals is even more difficult than the direct measurement of OH radicals. Thirdly, despite their low mixing ratios, certain NMHCs do play an

important role in the chemistry of the atmosphere. Namely, the enormous amounts of, e.g., isoprene emitted by vegetation not only affect the oxidative state of large air masses, and are precursors for O<sub>3</sub>, but also influence the formation of particles, which in itself has a range of climate-related effects.<sup>5</sup>

Although isotopic analysis of atmospheric gases has been increasingly applied over the last decades, the recent development of continuous flow mass spectrometry signals a true revolution, because it couples the widely used gas chromatography (GC) with isotope analysis. Thanks to this, in addition to CO<sub>2</sub>, H<sub>2</sub>O, CH<sub>4</sub>, CO, N<sub>2</sub>O, SO<sub>2</sub>, O<sub>2</sub>, HCHO, and H<sub>2</sub>, which have been analysed over the past decades, recently certain NMHCs have been subjected to <sup>13</sup>C-isotope analysis.<sup>18,19</sup>

There are good reasons to apply isotope analysis to NMHCs. Concentration measurements of NMHCs already are being used as a chemical clock. By comparing the rates of removal of a set of NMHCs from the atmosphere, the ages of air masses have been determined. Also the variability of NMHCs provides information about the rate of removal from the atmosphere. However, even though the concentration measurement of a single NMHC by itself does not give information about the portion of this gas removed by OH, isotope measurements may allow such inference. That is because the chemical loss processes by OH, O<sub>3</sub> and photolysis are accompanied by kinetic isotope effects (KIEs), and thus

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information pertaining to the degree of gas removal by a loss process may be provided. To some degree the isotope ratio forms an internal molecular chemical clock.

We did mention the  $^{13}\text{C}$  measurement of NMHCs, but measurement of the D/H ratio of NMHCs promises to be far more useful. The reason is that the reaction mechanism for reaction of OH with most NMHCs is that of H-atom abstraction, which induces a KIE that is larger than the KIE for  $^{13}\text{C}$ . Taking  $\text{CH}_4$  as an example, which admittedly is an extreme case, the KIE for D is 227%, which is much larger than the  $^{13}\text{C}$  KIE of 5% only.<sup>20</sup> The advantage of a large KIE is that in comparison the isotope variations due to source differences are smaller. Thus, although D isotope variations due to source differences cannot be excluded, they are in relative terms less important. This is important because the source isotopic composition of trace gases present in a certain air mass (by which we mean the isotopic composition of the trace gas at its source of origin) is usually not well known, which has hampered progress in quantitative applications.

Tremendous analytical improvements in mass spectrometry and the development of continuous flow isotope ratio mass spectrometry (CF-IRMS), in which very small gas samples can be isotopically analysed by introduction into the isotope mass spectrometer in a flow of He, have paved the way for a wider scale of application of isotope analysis in atmospheric chemistry. However, despite the orders of magnitude decrease in sample size brought about by the use of CF-IRMS, the concentrations of NMHCs in the atmosphere are, apart from source regions (e.g. boundary layer air over vegetation, or polluted city air), still at the low end for CF-IRMS applications. Bearing in mind that many hydrocarbons of interest do have short lifetimes, very low concentrations in the pmol/mol range are not uncommon.

Rudolph *et al.*<sup>21</sup> and Tsunogai *et al.*<sup>22</sup> report the  $^{13}\text{C}$ -isotope analysis of NMHCs ( $\text{C}_2\text{-C}_5$ ) using 5–10 L of air. To determine the D/H ratio much more air will be required. One reason is that the amount of D (0.015 or 0.03% for molecular hydrogen) is smaller than that of  $^{13}\text{C}$  (1.1%). The other reason has to do with the analytical method. For  $^{13}\text{C}$  analysis, the NMHC to be assayed is combusted to  $\text{CO}_2$ . For D/H analysis, however, the NMHC has to be converted into molecular hydrogen. Because the ionisation efficiency of  $\text{H}_2$  in the ion source of the mass spectrometer is smaller than that of  $\text{CO}_2$ ,<sup>23,24</sup> larger amounts of NMHC are required for D isotope analysis.

In this paper we report progress in separating NMHCs from large air samples. This is essential for attaining the ultimate aim of performing CF-IRMS measurements on some of the most valuable NMHCs. The large air samples discussed here are mostly from the routine measurement flights of the CARIBIC Boeing 767 passenger aircraft (for details, see the website<sup>25</sup>). A procedure we have used over the years to extract CO from large air samples for  $^{14}\text{C}$  analyses embraced the cryogenic separation of condensable gases followed by their recovery and storage. In the present paper we report several tests aimed at investigating which NMHCs have been successfully extracted this way, and how well they are preserved in flame-sealed ampoules. As we will show in the following, the extraction of NMHCs from large air samples appears to be relatively straightforward, although interesting effects are noted.

## EXPERIMENTAL

### Cryogenic concentration using large air samples

The only routine application we are aware of that involves the processing of very large air samples is the determination of the abundance of  $^{14}\text{C}$  in the atmosphere.<sup>26–28</sup> The concentration of  $^{14}\text{C}$  in tropospheric air ranges between a mere 5 and 25 molecules per  $\text{cm}^3$  STP. This is equivalent to  $2\text{--}10 \times 10^{-7}$  pmol/mol. The amount of air required for  $^{14}\text{C}$  analysis is at least 100 L (about 1 million  $^{14}\text{C}$  atoms) and typically about 300 L of air.

The procedure for  $^{14}\text{C}$  determination in air (and  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  of CO) is based on three preparative steps. First, all  $\text{CO}_2$  and other condensables are stripped by cryogenic trapping from a flow of sample air. Subsequently, the air containing basically only the reactive trace gases  $\text{CH}_4$  and CO (50 to a few hundred nmol/mol) is passed through a reactor with Schütze reagent ( $\text{I}_2\text{O}_5$  on acidified silica gel), which selectively oxidises CO to  $\text{CO}_2$ . The third step is the cryogenic trapping and recovery of the trace of CO derived  $\text{CO}_2$  (typically 10–100  $\mu\text{L}$ ).

In view of the low abundance of CO, it is absolutely essential that all  $\text{CO}_2$  is removed in the first step. For this purpose Russian doll traps (RDTs) have been developed.<sup>29,30</sup> Such traps are submerged in liquid nitrogen and contain two or three nested concentric borosilicate glass fibre thimbles whereon the condensation takes place. By using two traps in series, the  $\text{CO}_2$  content of the air is reduced to less than 0.5 nmol/mol at a flow rate of 5 L/min or even more.  $\text{CO}_2$  and  $\text{NO}_2$  as well as water vapour are for over 99% retained in the first of the two RDTs used. The extract from this trap (typically  $\sim 100\text{ cm}^3$ ) is used to measure the isotopic composition of  $\text{CO}_2$  in the aircraft samples.

The high efficiency of the RDTs for extracting  $\text{CO}_2$  makes it plausible that various hydrocarbons are also trapped quantitatively, although one would not expect to quantitatively recover traces of, e.g., ethane because of its relatively high vapour pressure compared with its very low partial pressure in ambient air. Moreover, it is not *a priori* clear that all trace gases are quantitatively released from the borosilicate glass surface. Problems are also to be expected in view of contamination as the  $\text{CO}_2$  extraction system with Viton O-ring glass valves (with small amounts of high vacuum grease) for processing air at a flow rate of 5 L/min is not necessarily of the ultra-high purity required for hydrocarbon analyses in general. Therefore, we have made a systematic study to ascertain to what degree extraction and recovery are quantitative, to what extent contamination does actually occur, and to what degree the NMHCs analysed remained unchanged in flame-sealed glass ampoules used to store these  $\text{CO}_2$  'concentrates'.

### Separation of gases on a CO extraction system

The samples dealt with were collected in the free troposphere using the CARIBIC Boeing 767-ER passenger aircraft flying from Holguin (Cuba) to Düsseldorf (Germany) on May 14, 2001, equipped with an automated air chemistry measurement container.<sup>25</sup> An air sampling system with membrane compressors and 12 large stainless steel canisters (each of 21 L volume) is integrated in the container for detailed

laboratory analysis of atmospheric trace gases directly after each measurement flight (analysed for CO, CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O, SF<sub>6</sub>, NMHCs and ~30 halogenated compounds). During the flight at an altitude of 10–11 km, the canisters are successively filled with air to ~17 bar.<sup>31</sup>

Upon return of the (bulky) aircraft air sample collector to the Max Planck Institute, it is connected via a 15 m long 1/4 inch o.d. stainless steel tube from the ground floor to the CO extraction system which is situated in a laboratory on the second floor. After flushing the tubing, three electro-polished stainless steel canisters of 2.5 L are filled with sample air. These aliquots have been used for NMHC and greenhouse gas analyses at the Max Planck Institute and halocarbon analyses at the University of East Anglia. Thereafter, the bulk of the air is processed by the CO extraction system following the three main steps described above.

The resulting CO<sub>2</sub> extracts are recovered after finishing a CO-extraction run. (The CO analysis is described in detail in the papers of Brenninkmeijer<sup>26</sup> and Brenninkmeijer *et al.*<sup>32</sup>) For this purpose, RDT-1 is isolated by closing the valves B1 and B3 (Fig. 1 does not show the entire CO extraction system, but only the relevant section), by opening B4 to the high vacuum pump (B5, B6, B8 are open) and pumping RDT-1 for about 7 min by which time most of the non-condensed gases (N<sub>2</sub> and O<sub>2</sub>) are removed. Next, the U-tube is cooled with liquid N<sub>2</sub> whilst the liquid N<sub>2</sub> used for cooling RDT-1 is removed. RDT-1 is simply left at ambient laboratory conditions (about 22°C) and pumped for ~35 min via the liquid N<sub>2</sub> cooled U-tube, after which B2 is closed. During this time CO<sub>2</sub> trapped in RDT-1 is transferred into the U-tube. Subsequently, the CO<sub>2</sub> extract is cryo-distilled from the U-tube into a glass bottle containing P<sub>2</sub>O<sub>5</sub> and is kept in this volume for ~2 min after warming to room temperature.

After this drying procedure the CO<sub>2</sub> extract is once more cryo-distilled, this time into a glass bottle with an O-ring valve. After MS determination (MAT-252, Finnigan, Germany) of the CO<sub>2</sub> isotopic composition, the extracts are cryo-distilled into glass ampoules and flame-sealed under

vacuum for long-term storage. (The ampoules were annealed at ~570 K under vacuum to remove in particular water.) Altogether, the CO<sub>2</sub> extract is transferred (by cryo-distillation) under vacuum four times. A Pirani vacuum gauge was used to observe and control each individual cryogenic transfer.

The time allowed for thawing the RDT was chosen to be 35 min. The recovery of CO<sub>2</sub> is found to be quantitative during 35 min as proven by test runs with variable thawing times. Using 35 min the main part of collected water traces remain trapped in RDT-1. Between runs, the entire CO extraction system is back-flushed with purified dry air, while other parts are evacuated.

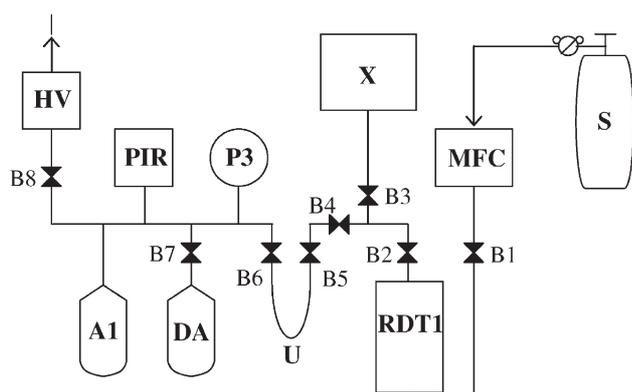
In order to answer the question how much CO<sub>2</sub> breaks through RDT-1 during a CO-extraction run, we isolated RDT-2 from the CO-extraction line and treated RDT-2 in the same way as described above for RDT-1, i.e. to recover all gases from RDT-2. Based on one measurement we calculate that less than 0.03% of all CO<sub>2</sub> escapes from RDT-1.

### Analysis of NMHCs and halocarbons in the diluted extracts

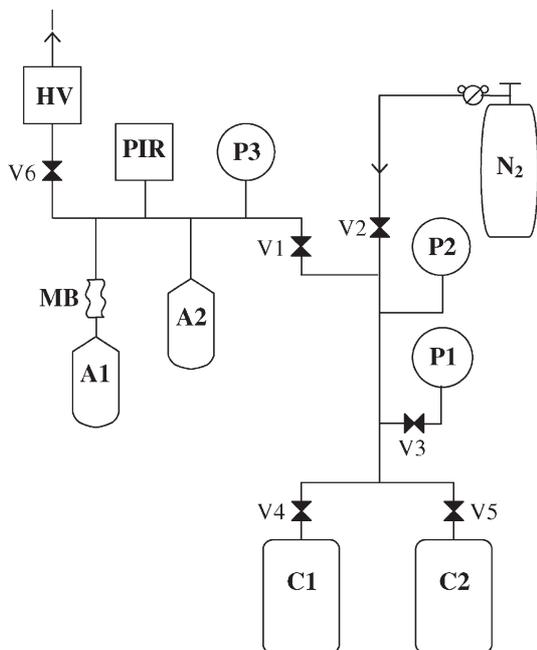
The NMHC and halocarbon analyses of the highly concentrated extracts (which have been stored for a few years in flame-sealed glass ampoules) are only possible after dilution with hydrocarbon-free air to obtain concentrations that are compatible with the GC system.

For this dilution, a clean vacuum line with glass valves (low-pressure part) and metal valves (high-pressure part) was used. First, the long neck of the glass ampoule (~100 cm<sup>3</sup>) is connected through a 1/4 inch Cajon Ultrator union and flexible bellows with the manifold shown in Fig. 2. The seal of the ampoule (A1) is broken inside the metal bellows and the extract is expanded into the pre-evacuated glass section of the manifold isolated from the metal section by V1. Next V1 is opened and a fraction is expanded into the metal section of the manifold. After V1 is closed again, one of the valves V4 and V5 is opened by which the fraction is subsequently further expanded into one of the 2.5 L pre-evacuated electro-polished stainless steel canisters C1 and C2, respectively. Each canister is filled to a pressure of about 6–7 mbar with the extract and this low-pressure reading is taken by using the MKS capacitance manometer (P1). After that the canister inlet is shut by valve V4 or V5, respectively. The unused extract is recovered by freezing it back into another, preconditioned 100 mL borosilicate glass ampoule (A2) immersed in liquid N<sub>2</sub> and flame-sealed for further storage. The manifold is evacuated again after which each of the SS canisters is separately pressurised with extra-pure nitrogen (6.0 grade) to a pressure of about 3.5 bar as measured using the second MKS capacitance manometer (P2). The canisters with mixture are left to homogenise for 1 day. The 6.0 grade nitrogen is additionally purified by a MS-gas purifier (Part No. 5182-3467, Hewlett Packard, USA). Impurities were proven to be below the detection limit by several blank runs.

The GC/MS systems used have been described elsewhere<sup>33–36</sup> and we give some details here only for NMHCs. After scavenging CO<sub>2</sub> by LiOH and H<sub>2</sub>O by Mg(ClO<sub>4</sub>)<sub>2</sub>, the condensables from 630 mL STP of air are cryogenically concentrated in a stainless steel microtrap (–170 C, 30 cm long, 0.76 mm i.d.) of which 10 cm are packed with porous



**Figure 1.** Schematic of the system used for extraction of CO and other condensable gases from air samples: HV, high-vacuum pump; S, sample bottle; PIR, Pirani vacuum gauge; MFC, mass flow controller; U, glass U-tube; A1, glass ampoule for the air extract; DA, finger with P<sub>2</sub>O<sub>5</sub> as drying agent; P3, piezoresistive pressure gauge; RDT1, Russian doll trap; B1–B8, Viton O-ring valves; X, the CO extraction system.<sup>32</sup>



**Figure 2.** The apparatus for diluting the extracts with high-purity air: HV, high-vacuum pump; N<sub>2</sub>, pressure bottle with pure nitrogen; A1, glass ampoule with the condensate; PIR, Pirani vacuum gauge, MB, metal bellows; A2, evacuated glass ampoule; C1, C2, stainless steel canisters; P1, MKS capacitance manometer (range 0–13 mbar); P2, MKS capacitance manometer (range 0–5 bar); P3, piezoresistive pressure gauge; V2–V5, bellow seal valves (Nupro, Swagelok); V1, V6, Viton O-ring valves.

silica beads (Unibeads 1S, 60/80 mesh, Alltech). The compounds were desorbed from the trap by heating from  $-170^{\circ}\text{C}$  to  $+150^{\circ}\text{C}$  within 3 s and introduced directly into the analytical GC column. The compounds are separated on a 50 m long Al<sub>2</sub>O<sub>3</sub>/KCl porous layer open tubular (PLOT) column (0.32 mm i.d., 5  $\mu\text{m}$ ) using a temperature programme starting at sub-ambient temperature (11 min  $10^{\circ}\text{C}$ , ramp  $5^{\circ}\text{C}/\text{min}$ , to  $200^{\circ}\text{C}$ ). The compounds are monitored by a quadrupole mass spectrometer operated in single ion monitoring mode and calibrated by a 30 compound certified gas mixture from the National Physical Laboratory (Teddington, UK). Importantly, the same instrument protocol, as well as the same calibration mixture, was used for analyses of NMHCs on original air samples and diluted extracts.

Halocarbons in the diluted extracts were analysed with the procedure adopted at UEA (University of East Anglia, Norwich, UK).<sup>34,35</sup> The analytical procedure involved cryogenic enrichment of 1000 mL air followed by chromatographic separation on a 100 m long column (DB5, 0.32 mm i.d., Agilent, USA) temperature programmed from 30 to  $200^{\circ}\text{C}$  using a bench-top quadrupole GC/MS system (Agilent 6890/5973). Again, the same instrument and protocol were used for halocarbon analyses on original air samples and diluted extracts.

In order to compare the mixing ratios measured for the diluted extracts with the data obtained in the past directly on the original whole air samples, both the enrichment factor (an enrichment of the extract relative the original air) and the dilution factor (dilution of the extract with 'zero' air) have to

be known. The enrichment factor was calculated by assuming condensates to be mainly CO<sub>2</sub> and N<sub>2</sub>O and taking the CO<sub>2</sub> content of the original air samples. The CO<sub>2</sub> content in the original air samples was analysed by an automated FID-GC system.<sup>37</sup> The enrichment factor was from 2672 to 2734. The dilution factor was calculated from pressure readings of the capacitance pressure gauges (P1, P2) and amounted from 495 to 505. The total uncertainty of the manometric dilution of the extract was 1.1%.

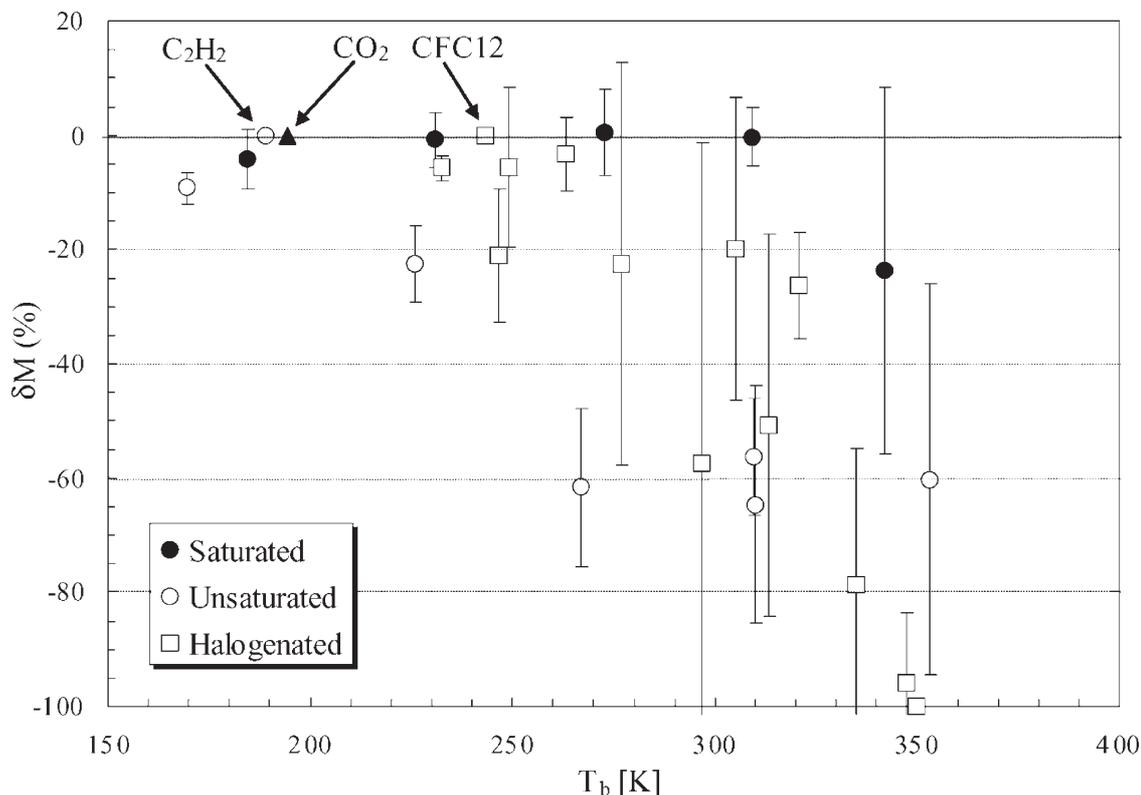
## RESULTS AND DISCUSSION

Four air samples collected during the CARIBIC flight # 33 from Holguin in Cuba back to Düsseldorf in Germany were selected for comparing results for the extracts with those for the original analyses performed in May 2001. The four samples # 2, 6, 9 and 12 represent the widest possible range in concentrations for this flight. Using propane which has a short chemical atmospheric lifetime as an indicator, the samples represent background tropical tropospheric air (# 2, with 69 ppt propane and # 12, with 95.5 ppt propane), upper tropospheric air polluted with boundary layer air (# 6, with 497 ppt propane) and stratospheric air (# 9, with only 17.4 ppt propane). For each of these four samples, 25 compounds embracing alkanes, alkenes and halocarbons were determined on the extracts in May 2003, after the dilution and measurement procedure described above.

No significant difference at the 95% confidence level was found for the C<sub>2</sub>–C<sub>5</sub> alkanes shown in Fig. 3 when using a test for detection of differences between the paired measurements,<sup>38</sup> i.e. between the direct analyses and analyses of extracts in our case.

In order to be able to compare the results, the data are plotted in Fig. 3 after normalisation using the ratio of C<sub>2</sub>H<sub>2</sub> for alkanes and alkenes, and CFC-12 (CF<sub>2</sub>Cl<sub>2</sub>) for the halocarbons for the extracts and original samples. This removes differences due to the dilution factor and possible changes in calibration. Furthermore, the normalised yield was averaged over the four samples. The plot shows, that within the substance class, the losses of each substance increase with increasing boiling point. In addition to that, unsaturated hydrocarbons and halocarbons are more prone to losses than alkanes. For the alkanes the recovery appears to be 100% up to C<sub>5</sub>, with a boiling point of  $\sim 310\text{ K}$ . For the unsaturated hydrocarbons and the halocarbons, recovery drops already for the compounds with boiling points as low as about 250 K.

A plausible explanation for the generally poorer recovery of the unsaturated hydrocarbons and the halocarbons as compared with the alkanes, and the correlation with the boiling point, is that these compounds have higher affinities for the filter material and may be retained on the borosilicate fibres of the thimbles inside the RDTs. The surface area of the thimble material is  $2\text{ m}^2/\text{g}$ , and glass is polar with many hydroxyl groups being present. Adsorption by P<sub>2</sub>O<sub>5</sub> used as a drying agent cannot be excluded as no separate experiments have been conducted. Loss of unsaturated compounds through reaction with ozone is unlikely. Ozone decays rapidly in metal canisters and most likely is not present in the CO<sub>2</sub>–matrix extracts. Furthermore, the cryogenic



**Figure 3.** Deviation from complete yield of NMHCs and halogenated carbons. The concentrations of hydrocarbons were normalised with the ratio of  $C_2H_2$  in the extract to that of direct analysis, the concentrations of halogenated compounds were normalised with the ratio of CFC-12 ( $CF_2Cl_2$ ). The points represent  $C_2$ – $C_6$  alkanes, ethene, propene, 1-butene, *trans*-2-pentene, *cis*-2-pentene, and benzene as unsaturated hydrocarbons, and HCFC-22 ( $CHClF_2$ ), HCFC-134a ( $CH_2FCF_3$ ),  $CH_3Cl$ , HCFC-142b ( $CF_2ClCH_3$ ),  $CH_3Br$ , CFC-11 ( $CFCl_3$ ), HCFC-141b ( $CFCl_2CH_3$ ),  $CH_2Cl_2$ , CFC-113 ( $CCl_2FCClF_2$ ),  $CHCl_3$ ,  $CH_3CCl_3$ , and  $CCl_4$  as halocarbons. Direct analyses of air samples taken during the CARIBIC flight # 33 from Holguin to Düsseldorf on May 14, 2001, were performed within 2 weeks after the flight, while the analyses of  $CO_2$  extracts were made in May 2003.

trapping of ozone from tropospheric air is notoriously difficult.<sup>39</sup>

While the recovery of higher boiling point compounds may be problematic, the recovery of the most volatile gases may depend on the degree to which they are trapped. For instance, ethene and ethane are the most volatile of all compounds measured here. Because their vapour pressures at liquid nitrogen temperature are high compared with their partial pressures, one would not expect ethene and ethane to be present at all in the extracts. Thus, although the release of ethene and ethane upon thawing of the RDTs is no problem, the trapping is not *a priori* to be expected. Certainly, in view of the four distillation steps, in which the efficient glass thimbles are not involved, the 100% yield for the  $C_2$  compounds is surprising. Therefore, we used other sample material to verify independently the remarkable recovery of ethane.

The comparison specifically for ethane is based on samples taken on board the Ron Brown NOAA research vessel during the INDOEX cruise in the Indian Ocean in February/March 1999.<sup>33</sup> Unlike the CARIBIC analyses made on aliquots of the same air sample, the direct INDOEX analyses were made on air samples taken in 2.5 L stainless steel canisters using a metal bellows pump and the extract analyses were made on air samples taken in 5 L high-pressure aluminium cylinders

pressurised by a modified RIX compressor.<sup>40</sup> Despite the different sampling periods of the sampling procedures, air samples were taken in fairly homogeneous air masses far away from emission sources and appear to be comparable. The results are summarised in Table 1. Again, at 95% confidence level,<sup>38</sup> the difference between the direct and the extract measurements is not significant. Ethane was not measured in the samples taken by the RIX compressor because these were contaminated during the sampling.

**Table 1.** Ethane mixing ratios in air samples from INDOEX measured directly and in  $CO_2$  extracts. The direct measurements were made in January 2000 whereas the analyses of  $CO_2$  extracts were carried out in May 2003

Sample pair	Ethane [pptv]		
	Direct	Extract	$\Delta$ [%]
31F/#5	540.2	556.1	2.9
35F/#6	647.0	659.6	1.9
49F/#8	752.0	688.5	-9.2
54F/#9	582.0	551.4	-5.5
67F/#11	180.8	196.8	8.1
71F/#12	373.3	328.5	-13.6
89F/#15	284.7	285.8	0.4
92F/#16	381.4	418.7	8.9

Because the partial vapour pressure of ethane in the air samples is lower than the vapour pressure at liquid nitrogen temperature, ethane cannot be condensed from air in a pure form. We postulate that CO<sub>2</sub> acts as a carrier gas during cryogenic transfer of the gas mixture and rapidly freezing CO<sub>2</sub> does trap ethane into a solid CO<sub>2</sub> matrix. Surprisingly, ethane is not pumped off when after each cryogenic gas transfer the frozen CO<sub>2</sub> matrix is left under vacuum for 1–2 min in order to remove non-condensable O<sub>2</sub> and N<sub>2</sub>. This effect is even more impressive when we consider C<sub>2</sub>H<sub>4</sub>, which not only has a higher vapour pressure, but an even lower partial pressure in air.

## CONCLUSIONS

Ultra-high efficiency cryogenic Russian doll traps (RDTs) routinely used to quantitatively trap CO<sub>2</sub> from large air samples are found to also quantitatively separate trace levels of C<sub>2</sub>–C<sub>5</sub> hydrocarbons and some halocarbons. The NMHCs recovered in the CO<sub>2</sub>–matrix extract are about 2700 times enriched relative to the original air samples. The NMHCs in CO<sub>2</sub>–matrix extracts that are flame-sealed in glass ampoules are found to be stable for more than 2 years.

A considerable decrease in recovery with increasing boiling point was observed for the unsaturated and halogenated compounds. This may be attributed to a higher affinity of these compounds towards the filter materials (borosilicate glass fibre) and/or the duration of trap thawing which is currently optimised for CO<sub>2</sub> isotope analysis (in which the transfer of water is minimised to exclude O isotope exchange between H<sub>2</sub>O and CO<sub>2</sub>). Further experiments will have to be conducted to ascertain whether the higher boiling point alkenes and halocarbons can be retrieved using the RDTs.

Nevertheless, the overall experience with the quantitative recovery of hydrocarbons in a CO<sub>2</sub> matrix from large air samples, and the unproblematic manipulation and storage of these 'extracts', shows that isotope analysis (including D/H) of several important NMHCs present in ambient air at very low levels will be possible.

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